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**RESEARCH REPORT No. CX-47**

# **Three-Body Recombination of Oxygen Atoms**

**ERNEST BAUER and MORRIS SALKOFF**

**Contract No. AF 19(604)4555**

**APRIL, 1960**

CX-47  
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THREE-BODY RECOMBINATION OF OXYGEN ATOMS

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The research reported in this paper has been sponsored by the Geophysics Research Directorate of the Air Force Cambridge Research Center, Air Research and Development Command, under Contract No. AF 19(60h)4555.

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## Abstract

We have made a quantum mechanical perturbed stationary state calculation of the rate of recombination of oxygen atoms in the presence of an oxygen molecule as third body. The recombination is considered to take place into highly excited vibrational levels ( $v = 9, 10$ ) of the  $A^3 \sum^+ u$  state of  $O_2$ . There are no adjustable parameters in the calculation: for the interaction potential we have used the results (for  $O_2 X^3 \sum_g^-$ ) obtained in a previous calculation, which were obtained by comparison with experimental measurements of vibrational relaxation times in oxygen. At temperatures of the order  $300 - 3000^\circ K$ , the calculated recombination coefficient into these two vibrational levels is of the order  $2 - 10 \times 10^{-33} \text{ cm}^6/\text{sec}$ , which agrees to within better than a factor of 3 with recent experimental measurements.

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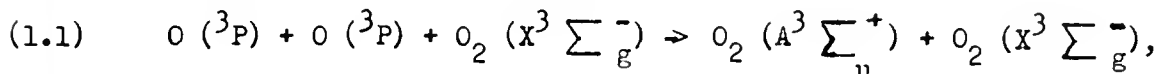


## 1. Introduction

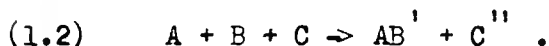
### a. Statement of the Problem

Two atoms can recombine to form a molecule in the presence of some third body such as an atom or molecule (or even a wall, but we shall not consider this case), or else radiatively. In practice, three-body non-radiative recombination is an important and interesting process which has considerable practical importance in the ionosphere, in shock wave relaxation, and in combustion; in fact three-body recombination is the prototype of an important class of chemical reactions.

For definiteness, we shall examine the recombination of two oxygen atoms in presence of an oxygen molecule -



which we shall write as



The primes indicate that the molecule AB is in general formed in an internally excited state, and the third body C may also carry away some internal excitation after impact.

It must be stressed that the present calculation is quite schematic; thus the detailed labeling  $O_2(A^3 \sum_u^+)$  is not to be taken too seriously. In fact, we have chosen this state because the vibrational levels of this state are known right up to the dissociation limit<sup>[1]</sup>. The purpose of the present calculation is to sketch the general order of magnitude of a three-body recombination process, rather than to make detailed calculations for one specific process.

We consider the case of a molecule AB formed in a highly vibrationally excited state, but do not consider the third body C to have any internal ex-

citation either before or after impact. On theoretical grounds [2,3] we believe that the molecule AB is very likely to be formed in a highly excited vibrational state, because in this way a minimum of energy has to be transferred into kinetic energy of C from the 'continuum' (i.e., unbound) vibration of A and B, and it is well known that the coupling of translational and vibrational energy is weak, so that energy transfer between these two modes of motion is difficult [4]. It should however be noted that thus far there appears to be no experimental evidence for the existence of such highly excited vibrational states [5]. The observations would be very difficult, but one should make further attempts to make the measurements, as well as to calculate the rate of degradation of vibrational energy in collisions.

Let us examine the implications of this model somewhat further. We may discount electronic excitation of either AB or C from adiabatic considerations (except in somewhat special situations that do not concern us here). Also, except in the special case of exact resonance, we may disregard any vibrational excitation of C after the collision, on account of the well-known difficulty of transferring relatively large amounts of energy between translation and vibration [4]. There remains the problem of rotational motion. It is clear that in most actual collisions there will be relative angular motion of AB and C, and the effects of this should certainly be examined. However, it is well known [4] that transfer of energy between translation and rotation is easy, and thus we feel that we can obtain an initial physical understanding of the situation by merely examining a collinear collision, in which rotational motion is disregarded. For definiteness we examine recombination into the two highest vibrational states,  $v = 9, 10$ .

#### b. The Present Model

We consider the collinear collision of two atoms A, B with a third



body C. The free atoms A,B are regarded as in the vibrational continuum of some electronic state of the molecule AB, and they fall into a bound, but still highly vibrationally excited, state of AB (still of the same electronic state of the molecule). The balance of the 'vibrational' energy of A and B is transferred into kinetic energy of the third body C, measured relative to the center of mass of AB. Thus we carry out a calculation of the transfer of energy between vibrational and translational degrees of freedom, analogous to earlier calculations of vibrational relaxation times in gases [6,7].

This is an adequate model within its very obvious physical limitations, but in practice we use a quantum mechanical perturbation method of calculation, the 'method of perturbed stationary states', which is adequate for vibrational relaxation processes (i.e., the  $v = 0$  to  $v = 1$  transition, which has a very small transition probability), but not for a process like three-body recombination, which is a very probable process. The situation is the following\*. One can calculate reaction rates classically, with a relatively detailed statistical model but only a crude estimate of transition probabilities [3,8,9], or else one can carry out a quantum mechanical calculation with a less detailed statistical model, but a better estimate of transition probabilities [10,11,12]. To get the complete story, one needs a synthesis of these two approaches: for processes having small transition probabilities the quantum method is better, while the classical approach gives more information for processes having large transition probabilities. Nevertheless, there are certain features that cannot be treated adequately by a simple classical model, such as the dependence of the cross section on the final state of vibrational excitation, and it is for this kind of detailed information that a calculation like the present one is useful.

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\*We should like to thank Dr. N. Davidson and Dr. J.C. Keck for some relevant remarks.

Thus it is necessary to examine the numerical results of the present work very carefully as a basis for improving one's general understanding of the problem.

It should be pointed out that in the present case the intermolecular potentials are known even less well than for the calculation of vibrational relaxation times<sup>[6,7]</sup>, but because the details of the quantum mechanical calculation are obscured by the large transition probability, this is not of the same importance as in other processes.

## 2. Calculation

### a. Method of Perturbed Stationary States

A rather thorough discussion of this method, and of the techniques of solution used here, has been given previously<sup>[6,16]</sup>. Call the two atoms that will combine A and B, and the third body C. Then we use the following coordinates, in which the motion of the center of mass separates off, and with which there are no cross terms in the kinetic energy -

$$(2.1) \quad \left\{ \begin{array}{l} \underline{\rho} = \underline{r}_A - \underline{r}_B \\ \underline{r} = \underline{r}_C - (M_A \underline{r}_A + M_B \underline{r}_B) / (M_A + M_B) \\ \underline{R} = (M_A \underline{r}_A + M_B \underline{r}_B + M_C \underline{r}_C) / (M_A + M_B + M_C) \end{array} \right.$$

If we separate off the motion of the center of mass in the coordinate  $\underline{R}$ , the wave equation becomes

$$(2.2) \quad (H_i(\underline{\rho}) + H_e(\underline{r}) + V^j(\underline{\rho}, \underline{r}) - E) \Psi_j(\underline{\rho}, \underline{r}) = 0; j = f, b,$$

where

$$(2.3) \quad \left\{ \begin{array}{l} H_i(\underline{\rho}) = - (\hbar^2 / 2M_i) \nabla_{\underline{\rho}}^2 + V_i^o(\underline{\rho}) ; M_i = M_A M_B / (M_A + M_B) \\ H_e(\underline{r}) = - (\hbar^2 / 2M_e) \nabla_{\underline{r}}^2 + V_e^o(\underline{r}) ; M_e = (M_A + M_B) M_C / (M_A + M_B + M_C) \end{array} \right.$$

'f' and 'b' stand for 'free' and 'bound' states respectively, while 'i' and 'e' stand for 'internal' (vibrational) and 'external' (translational) motion.

We solve the wave equation (2.2) by the 'method of perturbed stationary states', in terms of the unperturbed Hamiltonian  $H_0 = H_i(\underline{\rho}) + H_e(\underline{r}) -$

$$(2.4) \quad \left\{ \begin{array}{l} (H_0 - E) \Psi_j(\underline{\rho}, \underline{r}) = 0 ; \Psi_j(\underline{\rho}, \underline{r}) = \phi_j(\underline{\rho}) \psi_j(\underline{r}) \\ \psi_j(\underline{r}) = \sum_{\ell=0}^{\infty} (1/r) \chi_{\ell}(k_j r) P_{\ell}(\cos \theta_j), \end{array} \right.$$

where  $\chi_{\ell}(k_j r)$  satisfies the radial equation

$$(2.5) \quad \left\{ \begin{array}{l} (d^2/dr^2 - \ell(\ell+1)/r^2 - 2M_e V_e^0(\underline{r})/\hbar^2 + k_j^2) \chi_{\ell}(k_j r) = 0 \\ \chi_{\ell}(k_j r) \rightarrow \cos(k_j r + \delta_{j,\ell}) \text{ as } r \rightarrow \infty. \end{array} \right.$$

Further, the total energy of the system E is given by the expression

$$(2.6) \quad E = \epsilon_j + \hbar^2 k_j^2 / 2M_e .$$

For our collinear problem the  $\rho$ -motion is one-dimensional, and the vibrational wave function  $\phi_j(\rho)$  is a solution of the appropriate vibrational wave equation -

$$(2.7) \quad (H_i(\rho) - \epsilon_j) \phi_j(\rho) = 0.$$

The cross section for the excitation of a molecule from a discrete (bound) vibrational state b into a continuum (free) state f is then given by the following expression -

$$(2.8) \quad \partial \sigma_{fb}(\epsilon) / \partial \epsilon_f = \pi |v'_{fb}(\ell)|^2 / k_b k_f ,$$

where

$$(2.9) \quad v'_{fb}(\ell) = \int \int d\rho \, dr \, \phi_f(\rho) \chi_{\ell}(k_f r) v'(\rho, r) \phi_b(\rho) \chi_{\ell}(k_b r).$$

The reason for defining the dissociation cross section per unit energy range

is that the continuum 'vibrational' wave function  $\phi_f(\rho)$  is normalized per unit energy range (cf. Section 2.d). The actual cross section for dissociation is simply obtained by integrating the expression (2.8) -

$$(2.10) \quad \sigma_{fb}(\ell; \epsilon_f) = \int_0^{\epsilon_f} d\epsilon_f' (\partial \sigma_{fb}(\ell; \epsilon_f') / \partial \epsilon_f').$$

The character of the dissociation or recombination transition, in which we pass from a bound vibrational state of discrete energy  $\epsilon_b$  ( $< 0$ ) into a free vibrational state of energy  $\epsilon_f = \hbar^2 p_f^2 / 2M_1$  (thus  $\epsilon_f > 0$ , i.e., the state f is a continuum state), should be examined a little further. The condition of conservation of energy is

$$(2.11) \quad E = (\hbar^2 / 2M_e) k_b^2 - |\epsilon_b| = (\hbar^2 / 2M_e) k_f^2 + (\hbar^2 / 2M_1) p_f^2.$$

In an actual situation we have a definite bound vibrational state b with a definite and fixed value of  $\epsilon_b$ . The value of  $\epsilon_f$  is not fixed, but covers some kind of statistical range (typically a Maxwell-Boltzmann distribution corresponding to the gas temperature). The incident 'external' momentum  $k_f$  also covers an independent statistical range - which will of course also be a Maxwell-Boltzmann distribution for the appropriate temperature in a typical situation. Thus, a characteristic way to specify energy conservation is as follows -  $\epsilon_b$  is fixed;  $\epsilon_f$  and  $k_f$  are treated as independent, and Eq. (2.11) then fixes the value of  $k_b$  for a given set of values of  $\epsilon_f$  and  $k_f$ . To obtain a temperature-averaged dissociation cross section or recombination coefficient, we thus have to carry out separate and independent Boltzmann averages over  $\epsilon_f$  and  $k_f$ .

b. The Translational Potential  $V_e^0$  and the Perturbation Potential  $V'$

As in our previous work<sup>[6,13]</sup>, we neglect the angular dependence of  $V(\underline{r})$ , and use a Morse potential to describe the r-dependence of  $V_e^0(r)$  and of

$V'(\rho, r)$ . The precise numerical values are derived from our previous work on oxygen [7] -

$$(2.12) \quad \left\{ \begin{array}{l} V_e^o(r) = U_e^o \left[ e^{-2a(r-d)} - e^{-a(r-d)} \right] , \\ U_e^o = 1.43 \times 10^{-3} \text{ e}^2/a_o ; a = 1.1 \text{ a}_o^{-1} ; d = 6.63 \text{ a}_o , \end{array} \right.$$

$$(2.13) \quad \left\{ \begin{array}{l} V'(\rho, r) = (\rho - \rho_o) U' a \left[ e^{-2a(r-z)} - e^{-a(r-z)} \right] \\ U' = 0.262 \times 10^{-3} \text{ e}^2/a_o ; z = 7.40 \text{ a}_o . \end{array} \right.$$

In deriving Eq. (2.13) [13], we have expanded  $V'$  in powers of  $(\rho - \rho_o)$  (where  $\rho_o$  is the equilibrium nuclear separation of the AB-molecule), and have discarded all but the first term. This has some justification for the vibrational relaxation time problem, since the mean amplitude of oscillation, and the anharmonicity, of the lowest vibrational states  $v = 0, 1$  is not large. The expansion is certainly not justified in the present case on any quantitative basis, any more than is neglect of the angular dependence of  $V(\underline{r})$ . However, it is certainly not clear that putting in added complexity is justified by our knowledge of intermolecular potentials, and in particular these simplifications are justified by the general spirit of the present calculation, which is to attempt to get a feel for the general characteristics of the problem with a minimal amount of numerical work.

### c. The Vibrational Motion

The vibrational levels of the  $A^3 \sum_u^+$  state of  $O_2$  are known with great accuracy ( see Table I [1]). Thus one could fit a Morse potential to the data; however, this leads to a rather complicated expression for the matrix element of  $(\rho - \rho_o)$  between the discrete and continuum states. In view of our very crude approximation to the perturbation potential, there is clearly

not much point in treating the internal motion in any very refined way.

Consequently we have approximated the potential function  $V_i^0(\rho)$  of the vibrational motion by a square well of depth  $D$ , the dissociation energy of the state  $A^3 \sum_u^+$ , and width  $L$ : the width  $L$  is chosen to meet the matching requirements of the WKB approximation to the wave function  $\phi_b(\rho)$  [14].

Define [14]

$$(2.14) \quad \hbar^2 P^2 / 2M_i = D + \epsilon_f ; \hbar^2 Q^2 / 2M_i = D - |\epsilon_b| .$$

Then for a square well of depth  $D$  and width  $L$ , which is strongly repulsive for  $\rho < \rho_1$ , the WKB wave functions are

$$(2.15) \quad \begin{cases} \phi_b(\rho) = N_b \cos [Q(\rho - \rho_1) - \pi/4] ; N_b^2 = 2/L + 1/Q \simeq 2/L \\ \phi_f(\rho) = N_f \cos [P(\rho - \rho_1) - \pi/4] ; N_f^2 = 2M_i / \pi \hbar^2 P , \end{cases}$$

where  $\phi_f(\rho)$  is thus normalized per unit energy range. For there to exist a bound state  $b$  of energy  $\epsilon_b$ , we must have the quantum condition

$$(2.16) \quad QL = (v + 1/2)\pi , v \text{ an integer (vibrational quantum number)}.$$

If we take  $\rho_1 \simeq \rho_0$ , where  $\rho_0$  is the equilibrium nuclear separation of the AB-molecule, then the matrix element of  $(\rho - \rho_0)$  between the initial and final states is given by the expression

$$(2.17) \quad (\rho - \rho_0)_{fb} = 1/2 N_f N_b \left[ \frac{(-1)^v \sin PL}{(P-Q)^2} - \frac{(-1)^v L \cos PL}{(P-Q)} - (P-Q)^{-2} \right] ,$$

where terms of order  $(P+Q)^{-1}$  and  $(P+Q)^{-2}$  have been neglected.

#### d. Flux Conservation

Some of the results obtained by the numerical perturbation method violate the condition of flux conservation. That is, if we write the cross section for dissociation as

$$(2.18) \quad \sigma_{fb} = \sum_{\ell=0}^{\infty} (2\ell + 1) \sigma_{fb}(\ell) ,$$

then

$$(2.19) \quad \sigma_{fb}(\ell) > \pi / k_b k_f \text{ for } \ell < \ell_{crit} ,$$

and  $\pi / k_b k_f$  is the maximum value permitted for an inelastic scattering cross section by flux conservation [15].

The fact that the perturbation method gives results that violate flux conservation is due to the relatively small energy transfer between translational and vibrational degrees of freedom, and the consequent strong coupling between these two modes of motion. For instance, similar difficulties involving violation of flux conservation are quite familiar in the case of elastic scattering of a particle by a center of force, where the exact solution is of the form

$$(2.20a) \quad \sigma(\ell) = (4\pi/k^2) \sin^2 \delta_{\ell} ,$$

while perturbation theory gives the result [16]

$$(2.20b) \quad \sigma(\ell) = (4\pi/k^2) \tan^2 \delta_{\ell} .$$

A simple way to get a result that may be meaningful if the numerical (perturbation) calculations violate flux conservation is to put

$$(2.21) \quad \sigma_{fb}^{corr}(\ell) = \begin{cases} \pi / k_b k_f & \text{for } \ell < \ell_{crit} \\ \sigma_{fb}^{pert}(\ell) & \text{for } \ell > \ell_{crit} \end{cases} ,$$

where  $\ell_{crit}$  is obtained from the numerical (perturbation) cross section

$\sigma_{fb}^{pert}(\ell)$  by using Eq. (2.19).

Another scheme that will give results very similar to those of

Eq. (2.21) is to replace it by

$$(2.21^*) \quad \sigma_{fb}^{corr}(\ell) = \begin{cases} \pi / k_b k_f & \text{for } \ell < \ell_{crit} \\ 0 & \text{for } \ell > \ell_{crit} \end{cases} .$$

### e. Three-Body Recombination Coefficient

When two atoms A,B combine from the 'free' state f of the molecule AB into the bound state b, in the presence of a third body C (to conserve energy and momentum), the number of recombinations per unit volume and unit time is given by

$$(2.22) \quad d n_{rec} / dt = C_{bf} n_A n_B n_C ,$$

where  $n_A, n_B, n_C$  are the numbers of A,B,C atoms per unit volume;  $C_{bf}$  is the three-body recombination coefficient.

Three-body recombination is the inverse process to dissociation of the molecule AB by collision with C, and thus the three-body recombination coefficient  $C_{bf}$  is related to the dissociation cross section  $\sigma_{fb}$  by the principle of detailed balance. In particular, for the reaction (1.2), the number of dissociations per unit volume per unit time is given by

$$(2.23) \quad d n_{diss} / dt = \sigma_{fb} (\hbar k_b / M_e) n_{AB} n_C .$$

In a state of statistical equilibrium,

$$(2.24) \quad d n_{diss} / dt = d n_{rec} / dt ,$$

so that

$$C_{bf} = (n_{AB} n_C / n_A n_B n_C) (\hbar k_b / M_e) \sigma_{fb} .$$

Now, from equilibrium considerations [17] we obtain the result



$$(2.26) \quad (n_{AB}, n_C / n_A n_B n_C) = \Gamma_{bf} = G_{AB}/B_A G_B (1 + \delta_{AB}) (4\pi^2 \rho_0^2 k_b / p_f k_f),$$

which is derived in Appendix A. For our process (1.1) we have  $\delta_{AB} = 1$ , and

$G_{AB} = 3 G_A G_B$ , so that

$$(2.27) \quad \Gamma_{bf} = 6 \pi^2 (\rho_0^2 k_b / p_f k_f) .$$

We are interested in the temperature-averaged three-body recombination coefficient. From the discussion below Eq. (2.11) we see that before the temperature averaging,  $C_{bf}$  depends on any two of  $(k_b, k_f, \epsilon_f)$ , because of the energy conservation relation linking these quantities. For definiteness, let us treat  $k_f$  and  $\epsilon_f$  as independent variables. Under normal conditions,  $k_f$  and  $\epsilon_f$  are separately and independently distributed in Maxwellian fashion characterized by a temperature  $T$ . Thus, integrating first over  $\epsilon_f$ , we get

$$(2.28) \quad \begin{cases} C_{bf}(k_f, \epsilon_{f,avT}) = \int d\epsilon_f \Gamma_{bf}(\hbar k_b / M_e) \sigma_{fb}(k_f, \epsilon_f) A \epsilon_f^{1/2} e^{-\epsilon_f / kT} \\ A = 2\pi / (\pi kT)^{3/2} , \end{cases}$$

and finally, carrying out the second Maxwell-Boltzmann average, we get

$$(2.29) \quad \begin{cases} C_{bf}(T) = A^* \int k_f^2 dk_f e^{-\hbar^2 k_f^2 / 2M_e kT} C_{bf}(k_f, \epsilon_{f,avT}) \\ A^* = 4\pi (\hbar^2 / 2\pi M_e kT)^{3/2} . \end{cases}$$

The integrations extend over  $0 < \epsilon_f < \infty$ ,  $0 < k_f < \infty$ ;  $\sigma_{fb}$  just vanishes for those values of  $(\epsilon_f, k_f)$  that do not satisfy energy conservation.

The actual numerical calculations were made by averaging over  $\epsilon_f$  and  $k_b$  - not  $k_f$  - with independent Maxwellian distributions. In practice, if one takes energy conservation into account correctly, this makes no essential

difference, and the numerical results in the present situation are certainly not affected. However, on physical grounds it seems better to average over  $k_f$  and  $\epsilon_f$  rather than over  $k_b$  and  $\epsilon_f^*$ .

#### f. A Simple Physical Model of the Recombination Coefficient

In a situation where perturbation theory fails because the predicted cross section is so large that it violates flux conservation, we can try to get a rough analytical estimate of  $\ell_{\text{crit}}$  of Eq. (2.19), and then use Eq. (2.21) to give a value of  $\sigma_{fb}$  and thus get  $C_{bf}$ .

Evidently if the intermolecular potential has some mean range  $R$ , then this gives us a critical angular momentum  $\ell_{\text{crit}}$  from the standard 'impact parameter' condition -

$$(2.30) \quad \hbar \ell_{\text{crit}} = \hbar k_b R .$$

If we make use of the fact that  $k_f \simeq k_b$  and substitute this and (2.30) in (2.21), we get the result

$$\sigma_{fb}(\epsilon_f, k_f) = \sum_{\ell=0}^{\ell_{\text{crit}}} (2\ell+1) (\pi/k_b^2) = \pi R^2 ,$$

and substituting this in Eq. (2.28), (2.29), we get

$$(2.32) \quad C_{bf}(v, T) = 24\pi^2 \rho_o^2 R^2 \hbar / (M_i M_e)^{1/2} .$$

We notice that the result (2.32) as written down is a function of temperature  $T$ , only insofar as it affects the effective range  $R$ , and of the vibrational state  $v$  only to the extent that it enters in  $\rho_o = \rho_o(v)$ . We do observe, however, that this-admittedly very rough-approximation indicates that  $C_{bf}$  increases with increasing  $v$  (which increases the effective  $\rho_o(v)$ ), and decreases with increasing temperature since the atoms can approach closer

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\*We should like to thank Dr. K. Takayanagi for pointing this out to us.

and closer.

To get a simple numerical estimate, let us put  $R = 7 a_0 \simeq d$  of Section 2.b, then from Table I we have  $\rho_0(v)$  for  $v = 9, 10$ , which gives

$$(2.33) \quad \begin{cases} C_{bf}^{app.}(v=9) = 6.4 \times 10^{-33} \text{ cm}^6/\text{sec} \\ C_{bf}^{app.}(v=10) = 8.0 \times 10^{-33} \text{ cm}^6/\text{sec} . \end{cases}$$

A number of approximate estimates of three-body recombination coefficients have been made by different people. The simplest sort of considerations - obtained virtually from dimensional analysis - give [17, 18]

$$(2.34) \quad C_{rec} \sim f R^5 \bar{v} ,$$

where  $\bar{v} = (8kT/\pi M)^{1/2}$  is the mean speed,  $M$  = reduced mass, and  $f$  is some kind of a probability factor. For  $f \sim 1$ ,  $R = 7 a_0$ ,  $\bar{v} = 10^5 \text{ cm/sec}$ , this gives

$$(2.35) \quad C_{rec} \sim 5 \times 10^{-33} \text{ cm}^6/\text{sec} .$$

### 3. Results

The results of the Univac calculation are given in Tables 2 and 3. They are compared in Figure 1 with the latest experimental results [19,20]. We see that the experimental and theoretical results agree to within a factor of 3, which is a very considerable improvement over previous detailed quantum mechanical calculations [2,14]. One thing that is demonstrated quite clearly by the calculations is that recombination will lead to vibrationally excited molecules. This has been predicted by the theorists for quite a long time [3,14], but thus far there is not very much definite experimental evidence for it [5].

To be more specific, it has ~~always~~ been hard on strictly theoretical

grounds to understand the large experimental values of recombination rates; the fact that the present calculations - which take due account of the limitations on cross sections imposed by flux conservation - still exceed the experimental values is thus an error in the right direction. This may be corrected by a more appropriate choice of intermolecular potential, perhaps, or by detailed considerations that might indicate that a certain fraction of  $O(^3P)$  atoms will recombine into some state such as  $O_2(X^3 \sum_g^-)$ , which might perhaps have a state with binding energy significantly greater than the state  $O_2(A^3 \sum_u^+; v=10)$ , thus giving a smaller effective recombination coefficient. Of course it must be stressed that the experimental data are subject to some errors, while the theoretical results certainly cannot be relied upon to within better than a factor of order 3, on account of uncertainties arising from such considerations as the intermolecular potentials or detailed knowledge of bound vibrational states. A further source of error in the present calculation is that the effects of molecular rotation are neglected and all collisions are treated as though the potential were the same as for a collinear collision - an obvious overestimate.

To sum up, it was clear from the outset that a calculation of a problem as complicated as three-body recombination could not aim to obtain detailed quantitative results because of all the various factors that enter when one really tries to take all relevant physical effects into account; and to make an estimate of these - even if one were willing to undertake the labor - would call for detailed experimental information that is simply not available. The present calculation is thus a schematic one using a greatly oversimplified model. However, within its obvious limitations the present calculation does indicate that the orders of magnitude obtained in the experiments can be explained in terms of 'conventionally reasonable' mechanisms.

There is one additional piece of information that can be obtained, and that relates to the temperature dependence of the recombination coefficient. We see that the experimental results<sup>[19]</sup> show very little temperature dependence. The calculated recombination rate into the state  $v = 10$  does not vary very strongly with temperature, but still there is a low temperature fall in the rate. A more uniform rate would result if one supposed that recombination occurs into a state with binding energy lower than the  $100 \text{ cm}^{-1}$  that has been used here for the state  $v = 10$ , or perhaps into several such states. It might just be possible to obtain information on such very weakly bound vibrational states from some considerations related to these.

#### Acknowledgments

We should like to thank Dr. James C. Keck (AVCO-Everett Research Laboratory), Dr. Kazuo Takayanagi (Saitama University) and Dr. Ta-You Wu (National Research Council of Canada) for their interest and help at various stages of this work.

## Appendix A. Detailed Balance

For the purpose of the present discussion, which seeks to obtain a relation between the dissociation cross section  $\sigma_{fb}$  and the three-body recombination coefficient  $C_{bf}$ , we consider that the molecule AB is formed with rotational energy

$$(A.1) \quad E_{\text{rot}} = (\hbar^2/2M_i) p_o^2 J(J+1) \quad .$$

This is very convenient for our present purpose, and does not conflict significantly with the spirit of the perturbation calculation, even though we only consider collinear collisions there. Thus, we may define  $E_{ie}$  as the net energy transferred between the 'internal' and 'external' degrees of freedom, and then conservation of energy gives the two relations

$$(A.2) \quad \begin{cases} (a) & E_{ie} = (\hbar^2/2M_e) (k_b^2 - k_f^2) \\ (b) & E_{ie} = (\hbar^2/2M_i) p_f^2 - E_{\text{rot}} + |\epsilon_b| \quad . \end{cases}$$

Now, both the dissociation cross section  $\sigma_{fb}$  and the recombination coefficient  $C_{bf}$  are purely atomic properties which are independent of any macroscopic properties of the system, such as whether or not it is in equilibrium, of the temperature, density, etc.; but just because of this fact we may obtain the detailed balance relation under equilibrium conditions, which makes the calculation quite simple<sup>[17]</sup>. While the temperature  $T$ , and explicit references to equilibrium conditions, enter into the course of the analysis, these quantities fall out before the final result.

Equilibrium considerations give the result<sup>[17]</sup>

$$(A.3) \quad \Gamma_{bf} = \frac{n_{AB} n_C}{n_A n_B n_C} = \frac{n_{AB}^{(tot)}}{n_A^{(tot)} n_B^{(tot)}} \cdot \frac{f_1(T, M_1) f_1(T, M_{AB})}{f_1(T, M_{AB}) f_2(T) f_3(T)} \cdot \frac{(2J+1)h^3}{4\pi^3 p_f^2 dp_f} \cdot \frac{(4\pi h^3 k_b^2 dk_b)}{(4\pi h^3 k_f^2 dk_f)},$$

where  $n_A^{(tot)}$ ,  $n_B^{(tot)}$ , etc. refer to the total number densities of A, B, etc.;  $n_A$ ,  $n_B$  etc. refer to the number densities for momenta  $p_f$ ,  $k_f$ , etc.  $f_1(T, M)$  is the translational partition function for a system of mass  $M$  at temperature  $T$ ,  $M_{AB} = (M_A + M_B)$   $f_2(T)$  is a rotational and  $f_3(T)$  a vibrational partition function. The term  $(2J + 1)$  arises from the rotational state of the molecule;  $h^3$  is the balance in the phase space volume factors arising between  $(AB + C)$  on the one hand, and  $(A+B+C)$  on the other. The other terms,  $(4\pi h^3 k_f^2 dk_f)$ , etc. are phase volume contributions.

We have assumed no change in the electronic state of the system. The total number densities  $n_A^{(tot)}$ .... are related in equilibrium by the reaction isochore [17] -

$$(A.4) \quad \frac{n_{AB}^{(tot)}}{n_A^{(tot)} n_B^{(tot)}} = \frac{G_{AB}}{(1+\delta_{AB}) G_A G_B} \cdot \frac{f_1(T, M_{AB}) f_2(T) f_3(T)}{f_1(T, M_{AB}) f_1(T, M_1)},$$

where  $G_A$ ,  $G_B$ ,  $G_{AB}$  are the electronic statistical weights of A, B, AB, and  $\delta_{AB} = 1$  if A and B are identical, and zero otherwise (nuclear symmetry factor).

Substituting Eq. (A.4) in (A.3) and cancelling out terms, we get the result -

$$(A.5) \quad \Gamma_{bf} = \frac{G_{AB}}{G_A G_B (1 + \delta_{AB})} \cdot \frac{2\pi^2}{p_f^2 dk_f} \cdot \frac{(2J + 1)}{k_f^2 dk_f} \cdot \frac{k_b^2 dk_b}{k_f^2 dk_f}.$$

To get rid of the differentials that arise from the phase space volume, we differentiate Eq. (A.2a), (A.2b), keeping  $E_{ie}$  and  $\epsilon_b$  constant; thus Eq. (A.2a)

and (A.2b) give, respectively,

$$(A.6a) \quad k_b dk_b = k_f dk_f ,$$

and

$$(A.6b) \quad p_f dp_f = (2J + 1) 2 \rho_o^2 .$$

Notice that to get two relations (A.6a), (A.6b) from the single condition of conservation of energy (2.11) we have made an additional assumption implicit in Eq. (A.2) and explicit in the differentiation. That is, the phase space surface over which the condition of detailed balance is applied is chosen so that  $E_{ie}$  is constant along it.

If one now substitutes Eq. (A.6) in (A.5), one gets the final result

$$(2.26) \quad \Gamma_{bf} = \frac{G_{AB} 4\pi^2 \rho_o^2 k_b}{G_A G_B (1+\delta_{AB}) p_f k_f} .$$



## Appendix B. Dissociation Rates

From our analysis it is quite easy to estimate the temperature-averaged dissociation rate  $k_{\text{diss}}(T)$ , which is just the temperature average of  $(\hbar k_b/M_e) \sigma_{fb}$ . The total rate of dissociation is

$$(B.1) \quad (d/dt) n_{\text{diss}} = k_{\text{diss}}(T) n_{AB}^{(\text{tot})} n_C^{(\text{tot})}.$$

From Eq. (2.23), and the standard result [17]

$$(B.2) \quad n_{AB} n_C (k_b, \epsilon_b) dk_b = n_{AB}^{(\text{tot})} n_C^{(\text{tot})} A^* k_b^2 dk_b e^{\hbar^2 k_b^2 / 2M_e kT - (D_o - |\epsilon_b|)/kT},$$

where the constant  $A^*$  comes from Eq. (2.29) and  $D_o$  is the dissociation energy of the ground state, we get the result

$$(B.3) \quad k_{\text{diss}}(T) = A^* e^{-(D_o - |\epsilon_b|)/kT} \int_{\hbar^2 k_b^2 / 2M_e = |\epsilon_b|}^{\infty} (\hbar k_b/M_e) \sigma_{fb}(k_b, \epsilon_{f,avT}) e^{-\hbar^2 k_b^2 / 2M_e kT} k_b^2 dk_b.$$

Notice that we have used  $\sigma_{fb}(k_b, \epsilon_{f,avT})$ , which is given by the expression -

$$(B.4) \quad \sigma_{fb}(k_b, \epsilon_{f,avT}) = A \int_0^{\infty} \sigma_{fb}(k_b, \epsilon_f) \epsilon_f^{1/2} e^{-\epsilon_f/kT} d\epsilon_f,$$

where  $A$  is defined in Eq. (2.28).

It is quite easy to get an expression for  $k_{\text{diss}}(T)$  in terms of the approximation scheme of Section 2.f, which already gives us effectively a value of  $\sigma_{fb}(k_b, \epsilon_{f,avT})$  - cf. Eq. (2.31) for instance. Thus we get the result

$$(B.5) \quad k_{\text{diss}}^{\text{app.}}(T) = \pi R^2 (8kT/\pi M_e)^{1/2} (1 + |\epsilon_b|/kT) e^{-D_o/kT}.$$

Note that this result has been worked out for the case when we carry out independent Boltzmann averages over  $\epsilon_f$  and  $k_b$ , rather than over  $\epsilon_f$  and  $k_f$ . In practice this should not make any significant numerical difference to the results.

Table 1. Highly Vibrationally Excited Levels of the  $A^3 \sum_u^+$  State of  $O_2$

vibrational quantum v	binding energy $ \epsilon_b(v) (\text{cm}^{-1})$	nuclear separation $\rho_o(v)(a_o)$
10	104	3.69
9	340	3.56
....	....	....
0	5570	2.90

Table 2. Numerical Results for the Capture Cross Section  $\sigma_{fb}(\epsilon_f)$

Vibrational state  $v = 10$

$k_b$	$P_f$	$\ell_{crit}$	$\sigma_{fb}(\epsilon_f)$
15	1	--	26
	2	40	81
	3	60	93
	4	↓	99
	5	↓	105
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20	1	--	53
	2	80	111
	3	(>100)	121
	4	↓	124
	5	↓	127
	6	↓	132
<hr/>			
25	1	60	72
	2	120	112
	3	(>140)	135
	4	↓	137
	5	↓	139
<hr/>			
30	1	100	73
	2	140	89
	3	(>160)	93
	4	↓	94
	5	↓	95

Vibrational state  $v = 9$

$k_b$	$P_f$	$\ell_{crit}$	$\sigma_{fb}(\epsilon_f)$
20	1	--	2.4
	2	--	8.1
	3	--	12.4
	4	--	15.2
<hr/>			
25	1	--	7.6
	2	--	27
	3	40	42
	4	60	51
<hr/>			
30	1	--	15.5
	2	80	46
	3	100	52
	4	100	54
	5	(>120)	56
<hr/>			
35	1	--	32
	2	120	68
	3	150	80
	4	150	81
	5	150	82

Table 2 - Continued

<u>v = 10</u>			
$k_b$	$P_f$	$\ell_{crit}$	$\sigma_{fb}(\epsilon_f)$
40	1	180	84
	3	210	108
	5	210	117
	7	(>240)	118
	9	↓	121

<u>v = 9</u>			
$k_b$	$P_f$	$\ell_{crit}$	$\sigma_{fb}(\epsilon_f)$
40	1	120	52
	3	180	86
	5	↓	93
	7	↓	96
50	1	180	68
	3	240	100
	5	(>270)	117
	7	↓	119

Notes

- (i) the units of  $k_b$ ,  $P_f$  are  $a_o^{-1}$ ;  $\sigma_{fb}(\epsilon_f)$  is measured in  $a_o^2$ .
- (ii) for the definition of  $\ell_{crit}$  see Eq. (2.19); see Eq. (3.1) for  $\sigma_{fb}(\epsilon_f)$  when there exists a value of  $\ell_{crit}$ , i.e. when flux conservation limits the cross section.
- (iii) a numerical value of  $\ell_{crit}$  in parentheses, e.g. (> 100) means that flux conservation was violated up to the highest value of  $\ell$  for which calculations were made. Effective values of  $\sigma_{fb}(\epsilon_f)$  could, however, be inferred from other results.

Table 3. Calculated Values of Three-Body Recombination Coefficients  $C_{bf}(T;v)$ .

$kT$ (ev)	$C_{bf}(T; v = 10)$ ( $\text{cm}^6/\text{sec}$ )	$C_{bf}(T; v = 9)$ ( $\text{cm}^6/\text{sec}$ )
.03	$(2.5 - 3.5)10^{-33}$	----
.10	$5.8 \times 10^{-33}$	$1.1 \times 10^{-33}$
.20	$6.3 \times 10^{-33}$	$2.3 \times 10^{-33}$
.30	$6.3 \times 10^{-33}$	$3.2 \times 10^{-33}$

Note - the values at  $kT = .03$  ev ( $350^\circ\text{K}$ ) are uncertain because there were not enough numerical results.

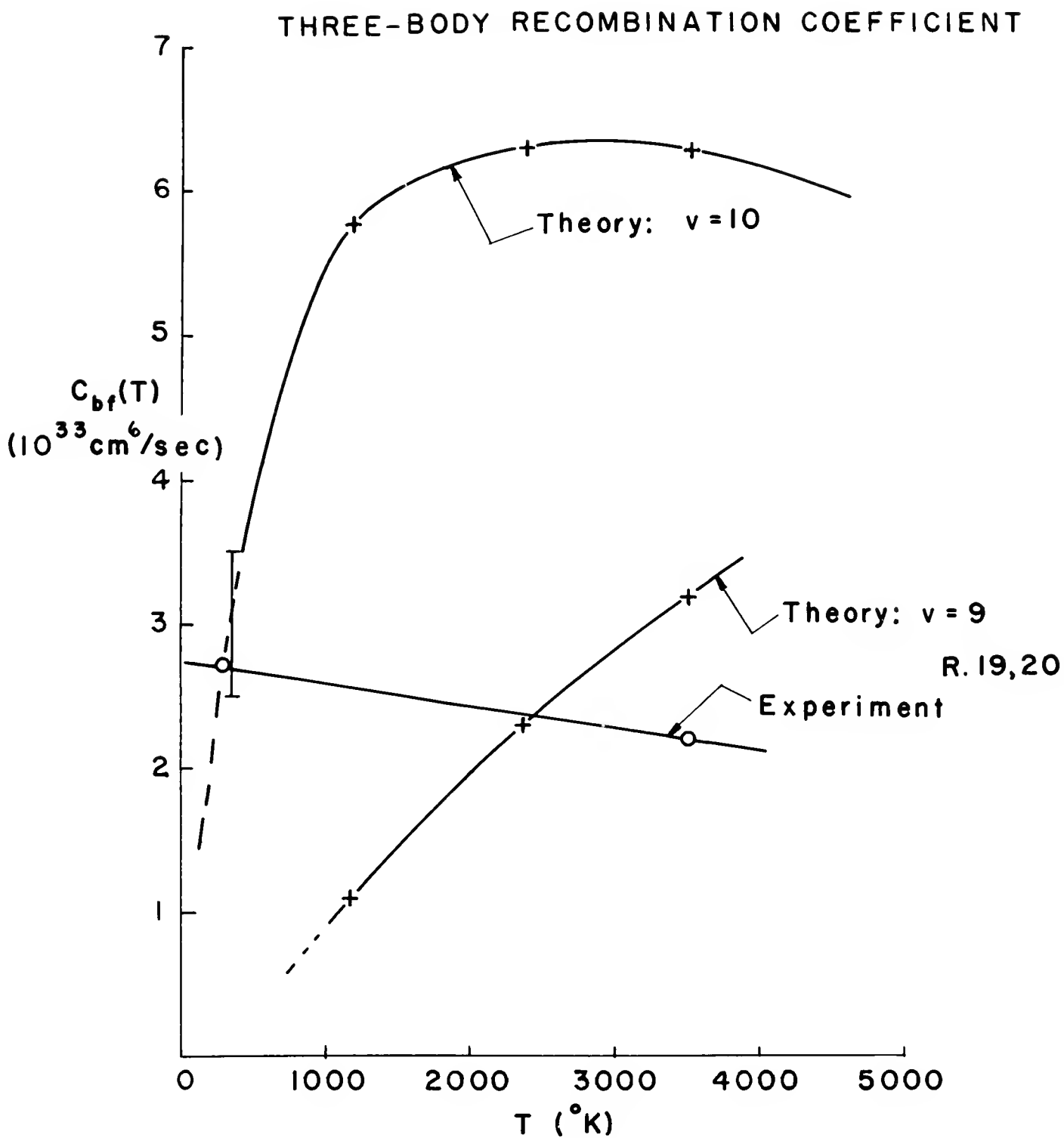


Figure 1

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\*We should like to thank Dr. Herzberg for a most helpful communication on this subject. See Brix and Herzberg, Can. J. Phys., 32, 110 (1954).

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## Research Reports and Publications

The following is a list of all research reports in the CX series:

CX-1	S. Borowitz	The Schwinger Variational Method for Three-Body Collisions <u>Published</u> - Borowitz and Friedman Phys. Rev., <u>89</u> , 441 (1953). Math. Rev., <u>14</u> , 756 (1953).	April '52
CX-2	H. Moses	A Self-Consistent Calculation of the Dissociation of Oxygen in the Upper Atmosphere <u>Published</u> - Phys. Rev., <u>87</u> , 628 (1952).	April '52
CX-3	K. Wildermuth	A Rigorous Solution of a Many-Body Problem <u>Published</u> - Acta Physica Austriaca, <u>7</u> , 299 (1953).	Aug. '52
CX-4	B. Friedman and E. Gerjuoy	Scattering Problems in Nonrelativistic Quantum Mechanics; Part I - One Particle in One Dimension	Dec. '52
CX-5	H. Moses	Exchange Scattering in a Three-Body Problem <u>Published</u> - Phys. Rev., <u>91</u> , 185 (1953). Math. Rev., <u>16</u> , 1186 (1955).	Jan. '53
CX-6	H. Moses	Formulation of the Kohn-Hulthén Variational Principle in Terms of the Scattering Operator Formalism <u>Published</u> - Phys. Rev., <u>92</u> , 817 (1953). Math. Rev., <u>15</u> , 587 (1954).	April '53
CX-7	H. Boyet and S. Borowitz	A Variational Calculation of the Elastic Scattering of Electrons by Hydrogen Atoms <u>Published</u> - Phys. Rev., <u>93</u> , 1225 (1954).	April '53
CX-8	H. Moses	A Self-Consistent Calculation of the Dissociation of Oxygen in the Upper Atmosphere; Part II- Three Body Recombinations <u>Published</u> - Phys. Rev., <u>91</u> , 1408 (1953).	April '53
CX-9	E. Bauer and Ta-You Wu	The Origin of the E-Layer of the Ionosphere <u>Published</u> - Phys. Rev., <u>92</u> , 1101 (1953).	July '53

CX-10	J.B. Keller	Derivation of the Bohr-Sommerfeld Quantum Conditions from an Asymptotic Solution of the Schrödinger Equation <u>Published</u> - Annals of Physics, <u>4</u> , 180 (1958).	July '53
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CX-13	H. Moses	The Scattering Operator in Quantum Mechanics; Part II- The Scattering Operator Formalism and Other Formalisms <u>Published</u> - (CX-12 and CX-13, portion of the material) Phys. Rev., <u>96</u> , 519 (1954). <u>Published</u> - (CX-12 and CX-13, summary) Il Nuovo Cimento, <u>1</u> , 103 (1955). Math. Rev., <u>16</u> , 1187 (1955).	Dec. '53
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CX-15	S. Schwebel	An Evaluation of Approximation Methods for Three-Body Scattering Problems <u>Published</u> - Phys. Rev., <u>103</u> , 814 (1956). Math. Rev., <u>16</u> , 1187 (1955). Math. Rev., <u>18</u> , 701 (1957).	May '54
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CX-19	H. Moses and I. Kay	The Determination of the Scattering Potential from the Spectral Measure Function; Part II- Point Eigenvalues and Proper Eigenfunctions  <u>Published</u> - Il Nuovo Cimento, <u>3</u> 66 (1956). Math. Rev., <u>17</u> , 155 (1956). Math. Rev., <u>17</u> , 740 (1956).	June '55
CX-20	H. Moses and I. Kay	The Determination of the Scattering Potential from the Spectral Measure Function; Part III - Calculation of the Scattering Potential from the Scattering Operator for the One- Dimensional Schrödinger Equation  <u>Published</u> - Il Nuovo Cimento, <u>3</u> , 276 (1956). Math. Rev., <u>17</u> , 489 (1956).	Sept. '55
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CX-22	S. Borowitz and M. Klein	A Perturbation Calculation of the Inelastic Scattering of Electrons by Hydrogen Atoms  <u>Published</u> - Phys. Rev., <u>103</u> , 612 (1956).	Nov. '55
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CX-27	H. Moses	The Kohn-Hulthén Variational Procedure for the Scattering Operator and the Reactance Operator; Part II - Procedures Independent of the Normalization of the Trial Functions  <u>Published</u> - Il Nuovo Cimento, <u>5</u> , 144 (1957). Math. Rev., <u>18</u> , 540 (1957).	July '56
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CX-44	L. Spruch, L. Rosenberg and T.F. O'Malley	Upper Bounds on Scattering Lengths When Composite Bound States Exist  <u>Accepted</u> - Phys. Rev.	Oct.'59
CX-45	P. Walsh and S. Borowitz	The Application of Wave Functions Containing Interelectron Coordinates. II. The Ground State Energy of Atoms  <u>Submitted</u> - Phys. Rev.	Dec.'59
CX-46	L. Spruch, L. Rosenberg and T.F. O'Malley	Upper Bounds on Electron-Atomic Hydrogen Scattering Lengths  <u>Submitted</u> - Phys. Rev.	Feb.'60

List of Publications Not Based on Reports

S. Borowitz      Three-Body Scattering Problems  
and B. Friedman

Phys. Rev., 93, 251 (1954).

S. Borowitz      Electron-Ion Recombination at  
Low Pressures

Trans. AIEE, 72, Part I, 430 (1953).

H. Moses          Calculation of the Scattering Potential  
from Reflection Coefficients

	Phy	Date Due		
J. Keller, I. Kay and J. Shmoys	Det Sca	JAN-18		
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Three-body recombination of  
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